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ELECTRICAL CONDUCTANCE IN ORGANIC SOLIDS

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ABSTRACT

This fourth quarterly progress report outlines the progress made on a two year program to study the electrical characteristics of some organic solids. The work is divided along three general lines: a) the study of transport of carriers injected into insulating (or poorly conducting) solids by an electron gun, b) electrical measurements on highly conducting ion-radical salts, and c) study of carrier transport in some amorphous systems.

During this quarter, the work has been centered on the first of these objectives. To this end, mobility and lifetime measurements for electrons and holes have been made on a series of single-crystal anthracene specimens. Good mobility data were obtained at room temperature on these samples, but severe trappings limited the lifetimes to ~50 microseconds. An attempt is being made to obtain crystals of higher purity and less trapping in order to extend the measurements to lower temperatures.

Initial efforts to observe carrier transport in NiO_2 (an inorganic narrow-band semiconductor with many similarities to the molecular crystal organic system) have been particularly encouraging. Significant multiplications, resulting in sufficient carrier generation, was observed in single-crystal samples. Arrival times were not observed, perhaps due to instrumental limitations in observing arrival times shorter than ~10 microseconds. The instrument is being modified to permit faster resolution.

The general direction and desired goals of this Program are covered in the Technical Proposal submitted by the Principal Investigators on June 26, 1963. As of this date, no changes in program or intent are envisioned. It was proposed that certain research problems in three areas would be investigated: a. carrier transport in organic systems using electron injection, b. some physical measurements on tetracyanoquinodimethan ion radical salts, and c. determination of carrier mobilities and trapping in amorphous systems. Work has been pursued in each of three areas by the two principal investigators working individually and/or jointly.

1. Anthracene

Using the electron-gun apparatus described in Quarterly Technical Report, 1 July 1964 to 30 September 1964, further efforts have been made to measure carrier mobilities in anthracene. Four more crystals, 25-mm diameter x 2-mm thick, were purchased from Harshaw Chemical Company. Preliminary to the electron-gun measurements, a qualitative transient photocurrent study was made for the purpose of determining the relative hole-electron photogeneration propensities of the crystals.

In a conventional "sandwich" cell (tin oxide coated quartz electrodes), the samples were exposed to a 0.2 microsecond light pulse - - strongly absorbed light of intensity sufficiently low to preclude space-charge-limited current at polarizing voltages up to 3000 volts. From these measurements, the relative quantum efficiencies for photocarrier generation were determined.

Table I

Sample	Hole	Electron
3	Poor	Poor
4	Low	Low
5	Very high	High
6	High	Undetectable

On the basis of this comparison, samples 5 and 6 were chosen for further study in the electron gun. The samples were fitted with opaque and transparent electrodes (using silver paint as described in the previous Quarterly Technical Report) and individually mounted in the electron-gun assembly.

Both samples exhibited large carrier multiplication when irradiated with beam electrons (>5-10 kv), with essentially equal electron and hole production -- showing that the generation mechanism is markedly different than for photocarrier production. Arrival times corresponding to mobilities of 0.1 → 1.0 cm^2/volt sec could be observed at polarization voltages up to 3000 volts. However, both samples exhibited severe trapping of electron and holes, reducing the lifetimes to ~50 microseconds and demonstrating a too high impurity concentration.

Here, in these room-temperature experiments, the transit arrival times and the corresponding mobilities can be measured. However, the relatively poor lifetimes (~50 microseconds) do not appear condusive to extending the measurements to low temperatures where trapping phenomena become even more severe. It is preferable o start with crystals of much higher purity.

D.C. Hoesterey, Eastman Kodak Company, has produced large

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1. D.C. Hoesterey and G.M. Setson, J. Phys. Chem. Solids 24, 1609 (1963).

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anthracene crystals exhibiting lifetimes of ~2000 microseconds. These crystals were produced by series of zone-melting passes in a manner too complex to reproduce within the tenure of this research program. Dr. Hoesterey was contacted with respect to obtaining a suitable sample for study -- such samples are not available at present, but should become available in early 1965.

2. Nickel Oxide

In the interim we are attempting to use the electron beam apparatus to measure hole and electron mobilities in NiO_2 single crystals grown in our laboratories by J.L. Weininger. The transport mechanism in the transition metal oxides is a matter of great theoretical interest, but no drift mobility data exist for any of these solids. From thermoelectric measurements on Li-doped NiO_2, Morin estimated a hole mobility of 10^{-4} cm^2/V-sec, but his interpretation is subject to many uncertainties. Two Hall effect experiments have been reported, one yielding a hole Hall mobility of 10^{-4}, the other a value of 1 cm^2/V-sec. The existing experimental results are therefore most inconclusive.

The crystals, obtained from Dr. Weininger, measure 10 X 10 X 0.5 mm. For the first experiments with these, electrodes were painted on with silver paint -- similar to the practice with anthracene -- even though it was recognized that the sample thinness precluded forming a grid of smaller dimensions. Later samples were fitted with evaporated gold electrodes, up to 300 A thick, which should be transparent to $>$ 10 keV electrons.

Marked multiplication was observed through the current enhancement at beam voltages of $>$ 5 eV. However, no induced current lasting longer than ~5 microseconds could be observed in the sample. It must be assumed therefore that the induced currents are either decayed or collected (at the opposite electrode) within the resolution time of the measuring electronics. At present, this time is limited to microseconds by band-pass filtering designed to minimize transient ringing and pick-up. This present lack of resolution makes a true evaluation impossible, but it appears that the mobility for electron-bombardment carriers in NiO_2 may indeed, be greater than, say 10^{-1} cm^2/volt sec. For example, if $\mu \approx 1$, then the arrival times would be less than 10 microseconds at the polarization voltages used. Smaller polarization voltages would, of course, lengthen the arrival times, but, also, reduce the signal strength proportionally.

The apparatus has now been modified in an attempt to provide faster resolving times and to increase the signal/noise ratio by the reduction of pick-up. A 50-ohm, shielded, terminated cable is used to couple the grid pulses to the gun. Both the shield and center conductor of the cable are connected to the pulser through 0.01μf, 30 KVDC capacitors. A transistorized, low-noise preamp has been furnished for initial, low-level amplification as close to the experiment as possible. Preliminary observations indicate considerable improvement in the operation of the system.